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# Application of Redfield theory to optical dephasing and line shape of electronic transitions in molecular mixed crystals

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Redfield relaxation theory is used to study optical dephasing in molecular mixed crystals where pseudolocalized phonons play a dominant role. As a model an effective four-level system is defined which consists of the ground and excited electronic state of the guest impurity and one pseudolocalized phonon in each of these states. It is shown that coherence transfer between the purely electronic and the phonon-promoted transition is due to interference between the scattering amplitudes in the ground and excited state and only occurs when the transitions are near resonant. When the scattering amplitudes in the ground and excited state are identical the optical Redfield equations reduce to the modified Bloch equations and coherence transfer may appreciably contribute to optical dephasing. It further proves essential for coherence exchange to occur that next to electron-phonon coupling the phonon anharmonicity is taken into account. The stochastic and correlation function theories of line shape, using the same model system, have also been examined and we conclude that in these theories exchange of coherence is not properly taken into account. Next to the effect of pseudolocalized phonons the effect of band phonons on optical dephasing is also examined and within our model both effects are additive.

## I. INTRODUCTION

With the recent success of coherent transient<sup>1-6</sup> and line narrowing (hole burning)<sup>7-11</sup> techniques in obtaining new information on the optical homogeneous line shape of electronic transitions in organic mixed crystals,<sup>12,13</sup> interest in this area has revived.<sup>14-17</sup>

Especially the finding that at low temperature the homogeneous linewidth<sup>1-3,11</sup> and shift<sup>11</sup> in several mixed crystals is exponentially activated, with phononlike activation energies, stimulated new activity. Prior to the optical domain such an exponential activation had been observed in the microwave domain by van 't Hof and Schmidt<sup>18</sup> and explained on the basis of the modified Bloch equations as introduced by McConnell.<sup>19</sup> The physical picture that emerged from this treatment was that the exponential activation of the homogeneous linewidth was due to exchange of coherence between the phononless and phonon promoted triplet spin transition. Harris and co-workers successfully carried this idea over into the optical domain and showed that dephasing of Frenkel excitons<sup>17</sup> and Raman dephasing<sup>20</sup> in molecular crystals might be explained on the basis of a stochastic model for the exchange of coherence.<sup>21-26</sup> Prior to this work, McCumber<sup>27</sup> also used stochastic exchange theory to describe narrowing effects of the zero-phonon-line in mixed crystals.

A different approach to the problem was made by Lubchenko *et al.*<sup>28-30</sup> and Krivoglaз<sup>31,32</sup> and more recently Abram<sup>16</sup> who, using the correlation function theory of line shape,<sup>33,34</sup> also derived line shape functions which showed the exponential activation property of the ZPL under some conditions.

As there are several theories for optical dephasing in mixed molecular crystals that predict qualitatively the same temperature behavior for the optical line shape, the question naturally arises, what is the relation between these theories and what are the limitations of each?

This question and the fact that, in our opinion, none of the existing theories for optical line shape gives a clear explanation of coherence transfer in terms of a microscopic model, stimulated us to a detailed study of the problem.

In this paper we present a theory for optical dephasing in molecular mixed crystals using Redfield relaxation<sup>35,36</sup> theory, which has previously been so successfully used in the field of magnetic resonance. A specific model is adopted, whereby the pseudolocalized phonons, which induce the exponentially activated relaxation effects, are treated on equal footing with the electronic levels. This approach seems justified as in several mixed crystals, the phonon side bands are as sharp as the purely electronic transition. Using the simplest possible model (four levels) the Redfield relaxation equations are derived.

It turns out that, in order to transfer coherence, it is essential that next to electron-phonon coupling the phonon anharmonicity is taken into account. Another interesting result is that exchange of coherence only occurs as a feeding term and is exclusively due to interference between the scattering amplitudes in the ground and excited state.<sup>37</sup> When these scattering amplitudes are identical the Redfield equations are shown to reduce to the modified Bloch equations. In the other limit where one of the scattering amplitudes dominates coherence transfer is negligible. It is further found that only between near-resonant transitions exchange can occur.

Comparison of Redfield theory with the stochastic and correlation function theory reveals that in the latter theories the interference character of exchange is not recognized and therefore not properly taken into account.

The paper is arranged as follows: The Hamiltonian that describes the model system is derived in Sec. II. Section III is devoted to the derivation of the Redfield equations describing relaxation in a four-level system. In Sec. IV the optical line shape on the basis of the Red-

field equations is calculated. In Sec. V it is shown that in certain limits this line shape function is identical to the one derived from the modified Bloch equations. In Sec. VI a comparison is made between the Redfield theory and the stochastic and correlation function theory of line shape. Finally, in Sec. VII the main conclusions of the paper are presented.

## II. THE MIXED-CRYSTAL MODEL HAMILTONIAN

### A. Introduction

As we are interested in the line shape (dephasing mechanism) of zero-phonon-lines (ZPL's) in the optical spectra of impurity centers in molecular solids we are interested in the Hamiltonian that describes the dynamic properties of such a system. The impurity is assumed to be embedded in an inert host crystal and its concentration is assumed low enough to neglect guest-guest interactions (energy transfer).

We further assume that the lowest electronic excitations of the guest molecule are not influenced by the host exciton bands; the host is therefore assumed to be inert, it only acts as a phonon reservoir. We therefore only consider the coupling of the local impurity electronic excitations to the phonons of the distorted (by substitution) host crystal. Insertion of an impurity into the pure host crystal causes the appearance of phonons of roughly three types.<sup>12</sup>

1. *Crystal or bandphonons.* These phonons correspond approximately with the allowed phononbands of the pure host crystal and have amplitudes of order  $N^{-1/2}$  on each atomic site. ( $N$  is the total number of atoms in the crystal.)

2. *Localized phonons.* Such phonons fall within the forbidden bands of the pure crystal and have considerable amplitudes (not depending on  $N$ ) on the impurity atoms only.

3. *Pseudo- or quasi-localized phonons (resonance phonons).* These phonons should be considered as finite wavepackets of bandphonons that hardly smear out over the crystal, but are confined to the atoms in a small area around the impurity. Compared to the bandmodes a substantial increase in amplitude on the guest will result.

In the Redfield, stochastic and correlation function theories to be discussed in the following sections we shall treat the (pseudo-) local modes separately from the bandphonon reservoir. We come back to this point in Sec. IID.

### B. The Born-Oppenheimer and harmonic approximation

The separate treatment of the electronic excitations and the phonons stems from the Born-Oppenheimer (BO) approximation.<sup>38</sup>

In the adiabatic BO approximation the electronic problem is solved first. The electronic energies obtained depend parametrically on the nuclear coordinates and serve as the potential surfaces (not necessarily parabolic) for the vibrational motions. As in general elec-

tronic excitation is accompanied by lattice deformation and force constant changes, these potentials will differ for each electronic state.

To proceed one quite often expands such a potential in a Taylor series around the equilibrium configuration for each electronic state. In the harmonic approximation one only retains the linear and quadratic terms which ensures diagonalization of the vibrational Hamiltonians.

In second quantization notation each electronic state ( $f$ ) is characterized then by its own phonon creation ( $b_{\kappa}^f$ ) and annihilation ( $b_{\kappa}^f$ ) operator for each mode with wave vector  $\kappa$  and frequency  $\omega_{\kappa}^f$ . It is customary,<sup>39</sup> however, to write the total Hamiltonian in terms of the electronic ground state phonon operators  $b_{\kappa}^*$ ,  $b_{\kappa}$  (where we suppressed the electronic ground state label).<sup>29</sup> So finally in the rotating wave approximation<sup>16</sup> the total Hamiltonian ( $H$ ) reads

$$\begin{aligned} H &= H_e^0 + H_p^0 + H_{e-p}^{0*}, \\ H_e^0 &= \sum_f \epsilon_f^f a_f^\dagger a_f, \\ H_p^0 &= \sum_{\kappa} \hbar \omega_{\kappa} (b_{\kappa}^* b_{\kappa} + 1/2), \\ H_{e-p}^{0*} &= \sum_{f, \kappa} V_{\kappa}^f (b_{\kappa} + b_{\kappa}^*) a_f^\dagger a_f + 1/2 \sum_{f, \kappa \kappa'} V_{\kappa \kappa'}^f (b_{\kappa}^* b_{\kappa'} + b_{\kappa} b_{\kappa'}^*) a_f^\dagger a_f \\ &\quad + \sum_{f \neq f'} i V_{ff', \kappa}^{N-BO} (b_{\kappa} - b_{\kappa}^*) a_f^\dagger a_{f'}, \\ &\quad + \sum_{f \neq f'} V_{ff', \kappa \kappa'}^{N-BO} (b_{\kappa}^* b_{\kappa'} + b_{\kappa} b_{\kappa'}^*) a_f^\dagger a_{f'}. \end{aligned} \quad (2.1)$$

In (2.1)  $a_f^\dagger$  ( $a_f$ ) denotes the creation (annihilation) operator for electronic state  $f$  with energy  $\epsilon_f^f$ .  $H_e^0$  and  $H_p^0$  consist, respectively, of the pure electronic and phonon contributions to the total energy.

The first two terms in  $H_{e-p}^{0*}$  are identified as the usual linear and quadratic electron-phonon interactions. They are due, respectively, to lattice deformation and phonon scrambling (nondiagonal quadratic terms) or frequency defects (diagonal) as a result of electronic excitation. Obviously in this model where the ground state is taken as the reference, they only act on excited states, e.g., e.g.,<sup>28-30</sup>  $V_{\kappa}^g = V_{\kappa \kappa'}^g = 0$ . Further note that these interactions only act *within* one particular electronic state.<sup>27,31</sup>

The third and fourth terms in  $H_{e-p}^{0*}$ , also represent linear and quadratic couplings. They, however, are linear and quadratic in the *momenta* of the nuclei (notice the minus sign<sup>40</sup>), not in their coordinates (plus sign). These terms are caused by a breakdown of the BO approximation and dynamically mix *different* (nearly-) degenerate electronic states, in contrast to the first two static couplings. Having established the quite different origins of these couplings,<sup>32,41,42</sup> it makes sense to treat them separately in order to avoid confusion.

As we shall consider only a (nondegenerate) electronic state with an energy  $\epsilon_f^f$  that substantially exceeds the maximum phonon energy, the "direct" (first order) phonon absorption and emission processes induced by non-BO couplings are forbidden by the law of conserva-

tion of energy. The probabilities for the multiphonon (higher order) processes will be assumed to be small. These processes change the difference in electronic energy into the energy of one or several phonons. We shall therefore omit the non-BO part of the interaction from (2.1) and only account for its effect by introducing<sup>31</sup> a radiationless rate constant  $\gamma_m$ .

Having modified (2.1) in this way, the reduced Hamiltonian, however, predicts the phonon lifetimes ( $\gamma_m^{-1}$ ) to be infinitely long in the electronic ground state. We shall therefore include the phonon anharmonicity to permit the decay of one phonon into several other ones.

### C. The phonon anharmonicity

Going beyond the harmonic approximation we take into account higher order terms than the quadratic in the Taylor series of the adiabatic potentials. Transforming again to ground state phonon operators, we arrive at the following Hamiltonian, whereby the phonon anharmonicity is included<sup>28-32</sup>:

$$\begin{aligned} H &= H_e^0 + H_p + H_{e-p}^0, \\ H_e^0 &= \sum_f \epsilon_f a_f^\dagger a_f, \\ H_p &= H_p^0 + H_{anh}, \\ H_p^0 &= \sum_{\kappa} \hbar \omega_{\kappa} (b_{\kappa}^\dagger b_{\kappa} + 1/2), \\ H_{anh} &= \frac{1}{3!} \sum_{\kappa\kappa'\kappa''} \{ U_{\kappa\kappa'\kappa''} b_{\kappa}^\dagger b_{\kappa'}^\dagger b_{\kappa''}^\dagger + \text{c.c.} \} + \dots \text{ similar terms}, \\ H_{e-p}^0 &= \sum_{f,\kappa} V_{\kappa}^f (b_{\kappa} + b_{\kappa}^\dagger) a_f^\dagger a_f + 1/2 \sum_{f,\kappa\kappa'} V_{\kappa\kappa'}^f (b_{\kappa}^\dagger b_{\kappa'} + b_{\kappa} b_{\kappa'}^\dagger) a_f^\dagger a_f. \end{aligned} \quad (2.2)$$

In (2.2) we have neglected cubic, quartic, etc., electron-phonon operators related to differences of the anharmonic potentials between the ground and excited electronic states. Similar to the linear and quadratic analogs, they would only affect excited states and would not mix different electronic states. Therefore the only effect is the addition of a pure anharmonicity-operator  $H_{anh}$  to  $H_p^0$ , yielding the total phonon-Hamiltonian  $H_p$ . Obviously  $H_{anh}$  only acts on phonon variables and is effective in *both* excited and ground states.

It will be more convenient<sup>36</sup> to redefine the electronic energy to include the thermal average of the interaction  $H_{e-p}^0$ :

$$H_e = H_e^0 + \langle H_{e-p}^0 \rangle_{th}, \quad (2.3)$$

$$H_{e-p} = H_{e-p}^0 - \langle H_{e-p}^0 \rangle_{th},$$

where

$$\langle H_{e-p}^0 \rangle_{th} = \text{Tr}(\rho_p^T H_{e-p}^0) \quad (2.4)$$

and

$$\rho_p^T = e^{-H_p/kT} / \text{Tr} e^{-H_p/kT}. \quad (2.5)$$

Here  $\rho_p^T$  is the reduced density operator for the (anharmonic) phonon bath, described by  $H_p$ . As a trace is independent of the representation in which it is evaluated, any complete set of phonon functions can be used to calculate the average (2.3). Using a harmonic basis set

the average phonon-occupation number  $\langle b_{\kappa}^\dagger b_{\kappa} \rangle_{th}$  yields the well-known expression<sup>28-31</sup>:

$$\bar{n}_{\kappa} = \langle b_{\kappa}^\dagger b_{\kappa} \rangle_{th} = [\exp(\hbar \tilde{\omega}_{\kappa} / kT) - 1]^{-1}, \quad (2.6)$$

where

$$\tilde{\omega}_{\kappa} = \omega_{\kappa} + \delta \omega_{\kappa},$$

and  $\delta \omega_{\kappa}$  is a small renormalization factor of the phonon frequency due to anharmonicity which will further be neglected, as we assume weak anharmonicity ( $\delta \omega_{\kappa}, \gamma_{\kappa} \ll \omega_{\kappa}$ ), so that  $\tilde{\omega}_{\kappa} \approx \omega_{\kappa}$ . Therefore the redefined Hamiltonian is

$$\begin{aligned} H &= H_e + H_p + H_{e-p}, \\ H_e &= \sum_f \left[ \epsilon_f + \sum_{\kappa} V_{\kappa}^f (\bar{n}_{\kappa} + 1/2) \right] a_f^\dagger a_f, \\ H_p &= \sum_{\kappa} \hbar \omega_{\kappa} (b_{\kappa}^\dagger b_{\kappa} + 1/2) \\ &\quad + \frac{1}{3!} \sum_{\kappa\kappa'\kappa''} [U_{\kappa\kappa'\kappa''} b_{\kappa}^\dagger b_{\kappa'}^\dagger b_{\kappa''}^\dagger + \text{c.c.}] + \dots, \\ H_{e-p} &= \sum_{f,\kappa} V_{\kappa}^f (b_{\kappa} + b_{\kappa}^\dagger) a_f^\dagger a_f + \sum_{f,\kappa} V_{\kappa}^f (b_{\kappa}^\dagger b_{\kappa} - \bar{n}_{\kappa}) a_f^\dagger a_f \\ &\quad + \sum_{\substack{f,\kappa\kappa' \\ (\kappa \neq \kappa')}} V_{\kappa\kappa'}^f b_{\kappa}^\dagger b_{\kappa'} a_f^\dagger a_f. \end{aligned} \quad (2.7)$$

In a first approximation the temperature-dependent shift of the Bohr frequency is immediately given by

$$\Delta \omega_{f,f'}(T) = \sum_{\kappa} [(V_{\kappa}^{f'} - V_{\kappa}^f) / \hbar] \bar{n}_{\kappa}. \quad (2.8)$$

In  $H_{e-p}$  the second and third term are the diagonal and nondiagonal quadratic electron-phonon coupling, representing fluctuations of the phonon occupation numbers and Raman scattering processes. For bandphonons the non-diagonal term will dominate the diagonal contribution ( $V_{\kappa}^f \sim 1/N$ ), while for localized phonons the reverse situation is expected.<sup>31,32</sup> These arguments led Lubchenko<sup>28-30</sup> and Krivoglaз<sup>31,32</sup> to treat the local phonons separately from the bandphonons, using a similar model as defined by (2.7).

In the following section we introduce a model, whereby the pseudolocal phonons fulfill a role similar to that of localized phonons.

### D. Model-Hamiltonian for an effective four-level system

Only very recently it has become clear<sup>2,3,9,11</sup> that pseudolocal phonons play a dominant role in the optical dephasing characteristics of molecular mixed crystals. As argued in Sec. II A, pseudolocalized phonons are expected to show substantial amplitudes on the guest site, and will therefore often behave as localized vibrations. It is further observed in several mixed crystals, e.g., tetracene in *p*-terphenyl,<sup>2</sup> that the hot pseudolocal phonon sideband can be as sharp as the ZPL. These considerations seem to justify the treatment of pseudolocalized phonons on equal footing with the electronic states.

Using the simplest possible model, we shall assume the existence of only one pseudolocalized phonon of frequency  $\Omega$ . Its operators will be denoted by capital let-

ters  $B^*$  and  $B$ , reserving the notation  $b_k^*$  and  $b_k$  for the bandphonons (we suppose localized phonons to be absent). We shall put all operators that solely contain pseudolocalized phonon variables ( $B^*, B$ ) into the unperturbed Hamiltonian  $H_e$ . For simplicity we only deal with a non-totally symmetric ( $u$ -) pseudolocal phonon, so that its linear electron-phonon coupling vanishes. This linear coupling induces the pseudolocal phonon side bands accompanying the ZPL in the impurity spectra and modifies the intensity of the ZPL, but hardly contributes to its width or shift.<sup>12,13</sup> In an harmonic approximation this contribution even vanishes (delta function), so that the above restriction is not severe. As a further simplifying assumption we omit the intrinsic anharmonicity of the pseudolocalized phonon. Rearrangement of (2.7) in this manner yields:

$$H = H_A + H_R + V_{AR},$$

$$H_A = \sum_f \left[ \epsilon_f' + \sum_k V_{fk}^f (\bar{n}_k + 1/2) + \hbar(\Omega + \Delta\Omega^f)(B^*B + 1/2) \right] a_f^\dagger a_f$$

$$H_R = \sum_k \hbar\omega_k (b_k^* b_k + 1/2) + \frac{1}{3!} \sum_{kk'k''} [U_{kk'k''} b_k^* b_{k'} b_{k''} + \text{c.c.}] + \dots,$$

$$V_{AR} = V_a + V_{e-p},$$

$$V_a = \frac{1}{3!} \sum_{kk'} [U_{kk'\lambda} b_k b_{k'}^* B^* + \text{c.c.}] + \dots, \quad (2.9)$$

$$V_{e-p} = \sum_{f,k} V_{fk}^f (b_k + b_k^*) a_f^\dagger a_f + \sum_{f,k} V_{fk}^f (b_k^* b_k - \bar{n}_k) a_f^\dagger a_f + \sum_{\substack{f,k,k' \\ (k \neq k')}} V_{fk'k}^f b_k^* b_{k'} a_f^\dagger a_f + \sum_{f,k} V_{fk\lambda}^f (b_k^* B + b_k B^*) a_f^\dagger a_f,$$

with  $\Delta\Omega^f = V_{\lambda\lambda}^f / \hbar$  and  $\Delta\Omega^e = V_{\lambda\lambda}^e / \hbar = 0$ . The index  $\lambda$  is used when the pseudolocalized phonon is involved. From (2.9) we extract the physical picture of the effective four-level system that will be studied in the next section.  $H_A$  describes what will be called the subsystem or "molecule." Here only the vibrationless ground state (labeled as level 1) and the lowest excited vibrationless electronic state (level 2) will be considered in conjunction with states of the pseudolocalized mode with one excited vibrational quantum (levels 3 and 4).

In Fig. 1 these four levels are depicted, where  $\Delta = \Delta\Omega^{f=2}$  represents the frequency-change of the pseudolocal phonon in going to the excited state. It is further assumed that only transitions from 1 to 2 and from 3 to 4 carry oscillator strength ( $S_1 - S_0$ ), with transition dipole moments of  $\mu_{12}$  and  $\mu_{34}$ , respectively. (Note that this choice implies that the pseudolocal phonon is of  $u$  symmetry).

$H_R$  represents the anharmonic bandphonon reservoir, while  $V_{AR}$  is the molecule-bath interaction consisting of an anharmonic ( $V_a$ ) and an electron-phonon coupling part ( $V_{e-p}$ ). Here  $V_a$  accounts for the decay of the pseudolocal phonon into several bandphonons.

The first three terms in  $V_{e-p}$  represent the electron-bandphonon coupling, while the last term is due to coupling of the band phonons with the pseudolocal phonon.

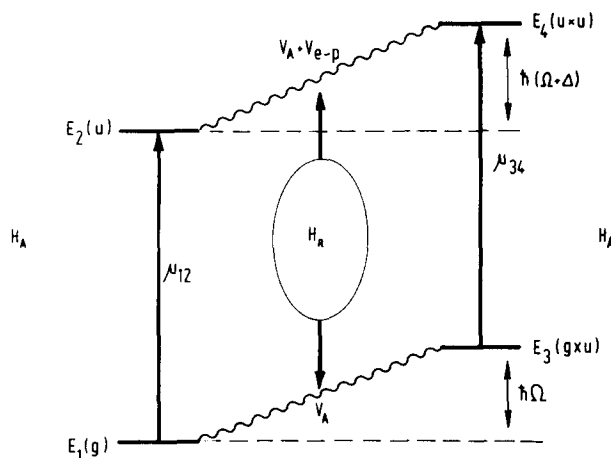


FIG. 1. Effective four-level system.  $E_1 = \epsilon^0 + \frac{1}{2}\hbar\Omega$ , ground state;  $E_2 = \epsilon' + \sum_k V_{kk'}^f (\bar{n}_k + \frac{1}{2}) + \frac{1}{2}\hbar(\Omega + \Delta)$ , excited state;  $E_3 = \epsilon^0 + \frac{3}{2}\hbar\Omega$ , ground state plus resonance phonon;  $E_4 = \epsilon' + \sum_k V_{kk'}^f (\bar{n}_k + \frac{1}{2}) + \frac{3}{2}\hbar(\Omega + \Delta)$ , excited state plus resonance phonon.

For the pseudolocal phonon both diagonal and nondiagonal quadratic electron-phonon coupling is expected to be important. Note that by the above procedure only the nondiagonal part appears in  $V_{e-p}$ , as the diagonal contribution is already contained in  $H_A$  by the frequency shift  $\Delta$ . The scattering among the two lowest levels and the two highest levels, providing the through-bath interaction of the purely electronic transition with the hot pseudolocal phonon transition (Fig. 1) is, respectively, induced by  $V_a$  and  $V_a + V_{e-p}$ . Therefore, in general the scattering in the electronic groundstate will differ from that in the excited state. Note further that all (BO) electron-phonon coupling terms neglected would also act on the excited state only.

The system-reservoir interaction operators are products of the type  $V_{AR} = AR$ , where  $A$  represents a molecule operator ( $a_f^\dagger, a_f, B^*, B$ ) and  $R$  a reservoir operator ( $b_k^*, b_k$ ). Because of the BO approximation the electronic operators commute with the phonon operators. Moreover, the pseudolocalized phonon operators commute with those of the bandphonons because of the boson commutation rules. This amounts to the statement that all molecule variables commute with the reservoir variables, Eq.  $[A, R] = 0$ .

In the next section it will be shown that the situation as sketched in Fig. 1 is amenable to application of optical Redfield theory.

### III. APPLICATION OF REDFIELD THEORY TO OPTICAL DEPHASING

In this section we will present a theory for optical dephasing in mixed molecular crystals where pseudolocalized phonons play a dominant role.<sup>2,3,9,11</sup> As was shown in the previous section, the total Hamiltonian of such a system may be written as  $H = H_A + H_R + V_{AR}$  (2.9). Within the approximations made,  $H_A$  describes the impurity ground and excited state and the pseudolocalized phonon levels.  $H_R$  generates the heatbath of delocalized crystal phonons and  $V_{AR}$  contains the interaction between the molecule

and the heatbath. Our motivation for partitioning the total Hamiltonian in this way is threefold.

First it enables us to employ Redfield relaxation theory<sup>35,36</sup> to study optical dephasing processes. Second, the dynamical equations obtained may be compared with McConnell's modified Bloch equations,<sup>19</sup> which recently were applied by Schmidt and van 't Hof<sup>18</sup> to the dephasing problem in the microwave regime (Sec. V). Third the line shape obtained from the optical Redfield equations (next section) may be compared with the results from other line shape theories, in particular the stochastic exchange theory of Anderson and Weiss<sup>21,22</sup> and Kubo,<sup>23-25</sup> as recently applied by Harris and co-workers,<sup>17,20</sup> and with the correlation function approach used by Krivog-laz,<sup>31,32</sup> Lubchenko,<sup>28-30</sup> and, more recently, of Abram.<sup>16</sup> This will be the subject of Sec. VI.

One additional remark on the Hamiltonian (2.9) should be made. The absence of an optical driving field term implies that we restrict ourselves to excitation processes where the (semiclassical) Rabi frequency  $(\mu_{ij}E_0/\hbar)$ , with  $\mu_{ij}$  the transition dipole and  $E_0$  the field amplitude at the molecule, is much smaller than the inverse of the correlation time  $(\tau_c^{-1})$  of the phonon heatbath correlation function. We thus ignore the effect(s) of the radiation field on the heatbath. We shall also neglect, temporarily, the effect of radiative and radiationless decay in our system. Its contribution to optical dephasing, however, may be added as a simple decay constant to the one obtained from phonon-scattering as these were supposed to be noninterfering decay processes. We finally note that the theory presented here is not new, but, to the best of our knowledge, has not previously been applied to optical relaxation processes in solids.

In our presentation of Redfield theory we shall closely follow Cohen-Tannoudji<sup>37</sup> who has given a very elegant derivation of the quantum-mechanical version of this theory. We shall not give a complete derivation, as this is given in Ref. 37, but instead, mention beneath the properties of our model that allow the usage of the main equations of this theory.

In the previous section we already remarked that in the Hamiltonian (2.9) all molecule variables commute with reservoir variables. As we assumed that only the molecule is driven by the optical field and the reservoir is in thermodynamical equilibrium, the total initial density matrix  $\rho(0)$  factorizes,  $\rho(0) = \rho_A(0)\rho_R(0)$ . Here  $\rho_A$  is the reduced density matrix for the molecule and  $\rho_R$  that for the reservoir, which is proportional to  $\exp(-H_R/kT)$ , so that it commutes with  $H_R$ .

Under these conditions, and if a perturbational treatment of  $V_{AR}$  is warranted, a master equation for  $\rho_A$  may be derived, describing the evolution of the molecule coupled to the large reservoir. In second order

$$\frac{d}{dt} \tilde{\rho}_A = -\frac{1}{\hbar^2} \int_0^t d\tau \{ \text{Tr}_R \tilde{\rho}_R(0) \tilde{R}(t) \tilde{R}(t-\tau) \} \\ \times \{ \tilde{A}(t) \tilde{A}(t-\tau) \tilde{\rho}_A(t-\tau) - \tilde{A}(t-\tau) \tilde{\rho}_A(t-\tau) \tilde{A}(t) \} + \text{c. c.} \quad (3.1)$$

The tilde ( $\sim$ ) stands for interaction representation.  $V_{AR}$  is written as a product of molecule ( $A$ ) and heatbath ( $R$ )

operators (see previous section), while  $\text{Tr}_R$  indicates tracing over heatbath states. In the derivation of (3.1) the first order term (which describes the effect of some sort of Hartree potential<sup>37</sup>) vanishes, because in (2.3) we defined  $V_{AR}$  in such a manner<sup>36</sup> that

$$\langle V_{AR} \rangle_{\text{th}} = \text{Tr} \rho_R V_{AR} = 0. \quad (3.2)$$

The basic approximation in the Redfield theory is the replacement in (3.1) of  $\tilde{\rho}_A(t-\tau)$  by  $\tilde{\rho}_A(t)$ , transforming (3.1) in a Markoffian equation. This approximation is justified only if the correlation time  $\tau_c$  of the heatbath function

$$G(\tau) = \text{Tr} \tilde{\rho}_R(0) \tilde{R}(t) R(t-\tau) = \sum_{\alpha\beta} p(\alpha) |\langle \alpha | R | \beta \rangle|^2 e^{i\omega_{\alpha\beta}\tau}, \quad (3.3)$$

is much shorter than the correlation time  $(T_2)$  of  $\tilde{\rho}_A(t)$ . Here  $G(\tau)$  is written explicitly in terms of heatbath states (Greek indices) and  $p(\alpha)$  is the probability of the heatbath to be in state  $\alpha$ .  $\tau_c$  corresponds to the inverse width of  $g(\omega)$ , which is the Fourier transform of  $G(\tau)$ . In our model  $g(\omega)$  represents the broad background of electron-phonon coupling and anharmonicity induced phonon transitions, which form the continuous spectrum accompanying the sharp ZPL. As this continuous spectrum generally extends over a region of tens of wave-numbers,  $\tau_c$  is in the subpicosecond regime and the above condition seems to be fulfilled. We note, however, that, as pointed out by Kenkre and Knox,<sup>43</sup> much of the *reversible* behavior of the system is removed by using the Markoffian approximation.

When information on  $\rho_A(t)$  is requested only on a time scale  $t \gg \tau_c$ , the master equation in the Schrödinger representation reduces to the following form in the basis of eigenstates (Latin indices) of the "molecular" Hamiltonian ( $H_A$ ):

$$\frac{d}{dt} \rho_{ij} = i\omega_{ij} \rho_{ij} + \sum_{im} \left[ \frac{-1}{\hbar^2} \int_0^\infty d\tau G(\tau) \left\{ \sum_{m'} e^{i\omega_{im'}\tau} A_{im'} A_{m'i} \delta_{mj} \right. \right. \\ \left. \left. + \sum_{i'} e^{i\omega_{i'm'}\tau} A_{m'i'} A_{i'i} \delta_{ij} - (e^{i\omega_{jm}\tau} + e^{-i\omega_{ji}\tau}) A_{ij} A_{mj} \right\} \right] \rho_{im}, \quad (3.4)$$

where  $\omega_{ij} = (E_i - E_j)/\hbar$  is an optical Bohr frequency and the index  $A$  of  $\rho_A$  is suppressed.

The first thing to note in the above master equation is, that the molecule-heatbath coupling may induce *transfer of coherence* between pairs of states in the molecule. The explicit dependence of this coherence transfer process on the heatbath states [through  $G(\tau)$ ], however, will be shown to *restrict* coherence transfer to near-resonant (*vide infra*) transitions. This result is not so surprising, as Fano in 1963<sup>44</sup> already showed that collisional induced transfer of coherence also only occurs between resonant transitions. Freed<sup>45</sup> has recently re-emphasized this point and noted, that resonant means, within the width of the states. We now wish to apply this formalism to the four-level system shown in Fig. 1.

Following Cohen-Tannoudji we may derive from Eq. (3.4) and Hamiltonian (2.9) a set of dynamical equations for the elements of the reduced density matrix, which will be used to determine the optical line shape. For the diagonal elements we find

$$\begin{aligned}
\dot{\rho}_{11} &= -\Gamma_{1-3}\rho_{11} + \Gamma_{3-1}\rho_{33}, \\
\dot{\rho}_{22} &= -\Gamma_{2-4}\rho_{22} + \Gamma_{4-2}\rho_{44}, \\
\dot{\rho}_{33} &= -\Gamma_{3-1}\rho_{33} + \Gamma_{1-3}\rho_{11}, \\
\dot{\rho}_{44} &= -\Gamma_{4-2}\rho_{44} + \Gamma_{2-4}\rho_{22},
\end{aligned} \quad (3.5)$$

where

$$\Gamma_{1-3} = \frac{2\pi}{\hbar} \sum_{\alpha\beta} p(\alpha) |\langle \alpha 1 | V_{AR} | \beta 3 \rangle|^2 \delta(E_{\alpha 1} - E_{\beta 3})$$

and

$$\Gamma_{2-4} = \frac{2\pi}{\hbar} \sum_{\alpha\beta} p(\alpha) |\langle \alpha 2 | V_{AR} | \beta 4 \rangle|^2 \delta(E_{\alpha 2} - E_{\beta 4}), \quad (3.6)$$

with

$$E_{\alpha 1} = E_{\alpha} + E_1$$

and similar expressions for  $\Gamma_{3-1}$  and  $\Gamma_{4-2}$  by interchanging the appropriate indices. For the nondiagonal elements we find

$$\dot{\rho}_{12} = -i(\omega_{12} + \Delta_{12}/\hbar)\rho_{12} - \Gamma_{12}\rho_{12} + \Gamma_{34-12}\rho_{34}, \quad (3.7a)$$

$$\dot{\rho}_{34} = -i(\omega_{34} + \Delta_{34}/\hbar)\rho_{34} - \Gamma_{34}\rho_{34} + \Gamma_{12-34}\rho_{12}, \quad (3.7b)$$

where  $\Delta_{12} = \Delta_1 - \Delta_2$

$$\begin{aligned}
\Delta_1 &= P \sum_{\alpha\beta} p(\alpha) \frac{|\langle \alpha 1 | V_{AR} | \beta k \rangle|^2}{E_{\alpha 1} - E_{\beta k}}, \\
\Delta_2 &= P \sum_{\alpha\beta} p(\alpha) \frac{|\langle \alpha 2 | V_{AR} | \beta k \rangle|^2}{E_{\alpha 2} - E_{\beta k}},
\end{aligned} \quad (3.8)$$

and a similar expression for  $\Delta_{34} = \Delta_3 - \Delta_4$  obtained by interchanging the indices 1 and 2 by 3 and 4, respectively.  $P$  indicates that the principal part should be taken. These second order shifts  $\Delta_{ij}$  [though temperature dependent through  $p(\alpha)$ ] are assumed to be small in comparison to the first order shifts (2.8) which are included in the definition of  $\omega_{12}$  and  $\omega_{34}$ , and lead to a renormalization of the transition frequencies.

The decay ( $\Gamma_{ij}$ ) and feeding ( $\Gamma_{ij-kl}$ ) constants take the following form:

$$\Gamma_{12} = \Gamma_{12}^{NA} + \Gamma_{12}^A, \quad (3.9a)$$

$$\Gamma_{12}^{NA} = \frac{1}{2}(\Gamma_{1-3} + \Gamma_{2-4})$$

$$\begin{aligned}
&= \frac{\pi}{\hbar} \sum_{\alpha\beta} p(\alpha) |\langle \alpha 1 | V_{AR} | \beta 3 \rangle|^2 \delta(E_{\alpha 1} - E_{\beta 3}) \\
&+ \frac{\pi}{\hbar} \sum_{\alpha\beta} p(\alpha) |\langle \alpha 2 | V_{AR} | \beta 4 \rangle|^2 \delta(E_{\alpha 2} - E_{\beta 4}),
\end{aligned} \quad (3.9b)$$

$$\begin{aligned}
\Gamma_{12}^A &= \frac{\pi}{\hbar} \sum_{\alpha} p(\alpha) \\
&\times \sum_{\beta} \delta(E_{\beta} - E_{\alpha}) |\langle \alpha 1 | V_{AR} | \beta 1 \rangle - \langle \alpha 2 | V_{AR} | \beta 2 \rangle|^2,
\end{aligned} \quad (3.9c)$$

$$\begin{aligned}
\Gamma_{34-12} &= \frac{\pi}{\hbar} \sum_{\alpha\beta} p(\alpha) \langle \beta 1 | V_{AR} | \alpha 3 \rangle \langle \alpha 4 | V_{AR} | \beta 2 \rangle \\
&\times \{ \delta(E_{\alpha 3} - E_{\beta 1}) + \delta(E_{\alpha 4} - E_{\beta 2}) \},
\end{aligned} \quad (3.9d)$$

and similar expressions for  $\Gamma_{34}$  and  $\Gamma_{12-34}$  obtained from the above by interchanging the indices 1, 2 by 3, 4.

Returning now to a discussion of the Redfield equa-

tions (3.5) and (3.7) we first note that, with our choice for  $V_{AR}$  in (2.9), the only nondiagonal elements that are coupled to each other are  $\rho_{12}$  and  $\rho_{34}$ . Except for the driving-field terms (which will be added later) these equations therefore have a form very similar to the modified Bloch equations postulated by McConnell.<sup>19</sup> The quantum-mechanical derivation of Eqs. (3.5) and (3.7), however, leads to new insight and restrictions in the use of these equations in the optical domain (Sec. IV).

A first important conclusion to be made is that *coherence transfer is negligible, unless the following relation holds:*

$$\Delta = |\omega_{12} - \omega_{34}| \lesssim \Gamma_{34-12}. \quad (3.10)$$

This condition follows directly from the energy conserving delta function in Eq. (3.9d) and from the prerequisite that  $\Gamma_{34-12} = \Gamma_{43-21}^*$ . Therefore in our description, up to second order in the perturbation expansion, only coherence transfer among near-resonant states is allowed.

A second important conclusion to be made is that Eqs. (3.9) show that coherence feeding and decay is due to distinctly different processes. In fact, the *coherence decay* itself is also due to two different types of effects. The first one, the adiabatic contribution denoted by  $\Gamma_{12}^A$  and  $\Gamma_{34}^A$  induces adiabatic (secular) transitions in the system. Consultation of Eq. (2.9) shows that the quadratic electron-bandphonon coupling,<sup>28-32</sup> which leads to elastic (within the linewidth<sup>27</sup>) Raman scattering processes, is responsible for the adiabatic contribution. A closer inspection reveals that this contribution is due to the *difference* of the independent *elastic* modulation of the initial and final state. These processes therefore can be classified as purely  $T_2$ -type processes. In the Debye approximation for the bandphonon density of states they lead to the well-known  $T^7$  and  $T^4$  temperature dependence of the width and shift, respectively, of the ZPL<sup>31,40,42</sup> at low temperature. The nonadiabatic (nonsecular) contributions  $\Gamma_{12}^{NA}$  and  $\Gamma_{34}^{NA}$  to the coherence decay are caused by inelastic  $T_1$ -type processes. Equation (2.9) shows that these inelastic scattering processes are induced by anharmonicity ( $V_A$ ) in the ground state and a combination of anharmonicity and electron-phonon coupling ( $V_{e-p}$ ) in the excited state. Here  $V_A$  describes the decay (creation) of the pseudolocalized phonon into (from) two bandphonons. The relevant part of  $V_{e-p}$  is in (2.9), the last term which describes in the excited state the exchange of a pseudolocalized phonon with a bandphonon. At low temperature ( $kT \ll \hbar\Omega$ ) we therefore expect the role of this last term to be negligible. Finally note that  $\Gamma_{ij}^{NA}$  is the *sum* of two *inelastic* phonon scattering processes in the ground and excited state.

We now turn to the *coherent feeding* term  $\Gamma_{ij-kl}$ . Equation (3.9d) shows that  $\Gamma_{ij-kl}$  is an *interference* term composed of the *inelastic* scattering amplitudes in the ground and excited state. Essential to the occurrence of coherence feeding in our model is therefore anharmonicity, as this provides a scattering mechanism that can act within both the electronic ground and excited state. It is also interesting to note that if the scattering

amplitude of one electronic state dominates that of the other, coherence transfer is negligible ( $\Gamma_{34-12} \ll \Gamma_{12}^{NA} \approx \Gamma_{12}$ ). In this case the optical Redfield relaxation equations (3.7a) and (3.7b) are no longer coupled and reduce to ordinary rate equations describing the incoherent decay. Such equations were previously used by Aartsma, Morsink, and Wiersma<sup>6</sup> for the interpretation of optical dephasing in the mixed crystal of tetracene in *p*-terphenyl under conditions, where the contribution of the bandphonons ( $\Gamma_{ij}^A$ ) could be neglected in comparison to that of the pseudolocal phonon. In the other limit where anharmonicity dominates, coherence transfer to a near-resonant pseudolocalized phonon transition may be important.

In conclusion of this section we shall derive some general relations among the decay and feeding constants under circumstances where the resonance condition (3.10) is fulfilled which implies:

$$E_4 - E_2 \approx E_3 - E_1 = \hbar\Omega. \quad (3.11)$$

As the heatbath is assumed to be in thermal equilibrium, the following relation holds<sup>37</sup>:

$$\Gamma_{i-1} = \exp[-(E_i - E_1)/kT] \Gamma_{i-1}. \quad (3.12)$$

This relation ensures that in thermal equilibrium the molecule and phonon populations will be given by the Boltzmann equilibrium law.

From (3.11) and (3.12) we infer the identities (neglecting radiative and nonradiative processes):

$$\Gamma_{1-3} = e^{-\hbar\Omega/kT} \Gamma_{3-1}, \quad (3.13a)$$

$$\Gamma_{2-4} = e^{-\hbar\Omega/kT} \Gamma_{4-2}, \quad (3.13b)$$

or

$$\Gamma_{12}^{NA} = e^{-\hbar\Omega/kT} \Gamma_{34}^{NA}, \quad (3.14)$$

$$\Gamma_{12-34} = e^{-\hbar\Omega/kT} \Gamma_{34-12}. \quad (3.15)$$

We shall use these relations in the following sections. We further note that in the following sections we only consider the effect of the pseudolocal phonons on the optical line shape. For a complete description of the line shape function the effect of the band phonons should be added.

#### IV. THE LOW TEMPERATURE ZERO PHONON LINE SHAPE OBTAINED FROM THE OPTICAL REDFIELD THEORY

In this section we will derive an expression for the optical line shape of a zero phonon electronic transition on basis of the Redfield equations (3.5) and (3.7) of the previous section, in the presence of an optical driving field.

At this point we note that the effect of radiative (and radiationless) decay can easily be incorporated in these equations by simply adding decay constants  $\gamma_{21}, \gamma_{23}, \gamma_{41}, \gamma_{43}$  to account for decay from excited state levels 2 and 4 to groundstate levels 1 and 2.

In the presence of a linearly polarized field  $E = E_0 \cos \omega t$  and using the electric dipole and rotating wave approximation,<sup>48</sup> the Redfield equations for the four-level

system (Fig. 1) become

$$\begin{aligned} \dot{\rho}_{11} &= \frac{1}{2}ik(\bar{\rho}_{21} - \bar{\rho}_{12}) - \Gamma_{1-3}\rho_{11} + \gamma_{21}\rho_{22} + \Gamma_{3-1}\rho_{33} + \gamma_{41}\rho_{44}, \\ \dot{\rho}_{22} &= -\frac{1}{2}ik(\bar{\rho}_{21} - \bar{\rho}_{12}) - (\Gamma_{2-4} + \gamma_{21} + \gamma_{23})\rho_{22} + \Gamma_{4-2}\rho_{44}, \\ \dot{\rho}_{12} &= \frac{1}{2}ik(\rho_{22} - \rho_{11}) + [i(\omega_0 - \omega) - \Gamma'_{12}]\bar{\rho}_{12} + \Gamma_{34-12}\bar{\rho}_{34}, \\ \dot{\rho}_{33} &= \frac{1}{2}ik(\bar{\rho}_{43} - \bar{\rho}_{34}) + \Gamma_{1-3}\rho_{11} + \gamma_{23}\rho_{22} + \Gamma_{3-1}\rho_{33} + \gamma_{43}\rho_{44}, \\ \dot{\rho}_{44} &= -\frac{1}{2}ik(\bar{\rho}_{43} - \bar{\rho}_{34}) + \Gamma_{2-4}\rho_{22} - (\Gamma_{4-2} + \gamma_{41} + \gamma_{43})\rho_{44}, \\ \dot{\bar{\rho}}_{34} &= \frac{1}{2}ik(\rho_{44} - \rho_{33}) + [i(\omega_0 + \Delta - \omega) - \Gamma'_{34}]\bar{\rho}_{34} + \Gamma_{12-34}\bar{\rho}_{12}, \end{aligned} \quad (4.1)$$

where we used the Condon approximation  $\mu_{12} = \mu_{34} = \mu$  and  $k = \mu E_0 / \hbar$ , ignored all second order shifts of the previous section, and where  $\bar{\rho}_{12} = \rho_{12} e^{-i\omega t}$ ,  $\bar{\rho}_{21} = \rho_{21} e^{+i\omega t}$  and similar expressions for  $\bar{\rho}_{34}$  and  $\bar{\rho}_{43}$ . We further substituted  $\omega_{21} = \omega_0$  and  $\omega_{43} = \omega_0 + \Delta$  and  $\Gamma'_{12} = \Gamma_{12} + \frac{1}{2}(\gamma_{21} + \gamma_{23})$ ,  $\Gamma'_{34} = \Gamma_{34} + \frac{1}{2}(\gamma_{41} + \gamma_{43})$ .

From Eqs. (4.1) an expression for the line shape is obtained under slow passage conditions, where the system is in steady state. Ignoring saturation effects, e.g.,  $k \ll \Delta$ , the populations will have their equilibrium values and we shall denote  $(\rho_{22} - \rho_{11})_{eq}$  and  $(\rho_{44} - \rho_{33})_{eq}$  by  $P_0$  and  $P_1$ , respectively. Under these conditions the line shape function, determined by  $\text{Im}[(\bar{\rho}_{12} + \bar{\rho}_{34})\mu]$ , is

$$\begin{aligned} \bar{\rho}_{12} + \bar{\rho}_{34} &= (\frac{1}{2}ik/N) \{ P_0 [\Gamma'_{34} + \Gamma_{12-34} - i(\omega_0 + \Delta - \omega)] \\ &\quad + P_1 [\Gamma'_{12} + \Gamma_{34-12} - i(\omega_0 - \omega)] \}, \end{aligned} \quad (4.2)$$

where

$$N = [\Gamma'_{12} - i(\omega_0 - \omega)][\Gamma'_{34} - i(\omega_0 + \Delta - \omega)] - \Gamma_{12-34}\Gamma_{34-12}.$$

We first note that, as long as condition (3.10) holds, this equation is valid at all temperatures for the four-level system.

As we wish to compare the results of our line shape calculation with those obtained from a stochastic<sup>17,20-26</sup> and correlation function approach<sup>28-32</sup> we investigate the ZPL line shape in the low temperature limit  $kT \ll \hbar\Omega$ , or  $P_1 \ll P_0$ . An analytic solution may be obtained if we consider the situation near the center of the ZPL, where  $(\omega_0 - \omega) \ll \Delta$ . In this limit the line shape function is only determined by the first term of Eq. (4.2) and it is easily shown that the line shape is purely Lorentzian.

For the full width at half-maximum  $[\pi T_2(T)]^{-1}$  we calculate the following expression:

$$[\pi T_2(T)]^{-1} = \left[ \Gamma'_{12} - \frac{(\Gamma'_{34})^{-1} \Gamma_{12-34} \Gamma_{34-12}}{1 + \Delta^2 (\Gamma'_{34})^{-2}} \right] (\text{sec}^{-1}). \quad (4.3)$$

The exchange terms are also shown to introduce a shift  $\Delta\omega_{ex}(T)$  of the absorption line, which is found to be

$$\Delta\omega_{ex}(T) = \frac{\Delta(\Gamma'_{34})^{-2} \Gamma_{12-34} \Gamma_{34-12}}{1 + \Delta^2 (\Gamma'_{34})^{-2}} (\text{rad sec}^{-1}). \quad (4.4)$$

At this point there are several interesting points to note.

First, the effect of radiative and radiationless decay on the line shape function can not trivially be separated from the effect of exchange. Second, neglecting these radiative and radiationless effects, or putting  $\Gamma'_{12} = \Gamma_{12}$  and  $\Gamma'_{34} = \Gamma_{34}$ , Eqs. (4.3) and (4.4) will show an exponential temperature dependence under the assumption that the heatbath is in thermodynamic equilibrium and when



only near-resonant states are considered, as then Eq. (3.15) is valid. Equations (4.3) and (4.4) then become:

$$[\pi T_2(T)]^{-1} = \left[ \Gamma_{12} - \frac{\Gamma_{34}^{-1} |\Gamma_{34-12}|^2 e^{-\hbar\Omega/kT}}{1 + \Delta^2 (\Gamma_{34})^{-2}} \right] (\text{sec}^{-1}), \quad (4.5)$$

$$\Delta\omega_{\text{ex}}(T) = \frac{\Delta(\Gamma_{34})^{-2} |\Gamma_{34-12}|^2 e^{-\hbar\Omega/kT}}{1 + \Delta^2 (\Gamma_{34})^{-2}} (\text{rad sec}^{-1}). \quad (4.6)$$

Third, Eqs. (4.5) and (4.6) only reduce to the ones derived by van 't Hof and Schmidt<sup>18</sup> and also by Harris<sup>17</sup> when, in addition, the scattering amplitudes in the ground and excited states are identical (see also Sec. V). Finally, there is no *a priori* reason to assume that  $\Gamma_{34}^{-1}$  [ $\tau$  in Ref. 18 is temperature independent. The full expression for  $\Gamma_{34}$  (Eq. (3.9)) indeed shows that it is a function of temperature through  $\rho(\alpha)$ . Careful measurement of the ratio between the temperature dependent broadening and shift ( $\Delta\Gamma_{34}^{-1}$ ) therefore should reveal this dependence. At higher temperatures, we emphasize this again, the full expression for the line shape function in Eq. (4.2) should be used.

We further note that in case of negligible exchange ( $\Gamma_{12-34} \ll \Gamma_{12}$ ) for both transitions, on basis of Eq. (4.2), also Lorentzian line shapes are predicted with widths determined by  $\Gamma_{12} + \gamma_R + \gamma_{NR}$  (where  $\gamma_R$  and  $\gamma_{NR}$  are the overall radiative and radiationless decay constants). In this case, however, there will be no temperature dependent shift induced by interaction with the pseudolocal phonon, and the shift will be induced by other processes, e.g., involving the crystal phonons.

We finally note that the Redfield equations are also applicable for a study of coherent transient effects, as photon echo and free induction decay. It is easily shown that, at low temperature, the damping of  $\rho_{12}(t)$  is governed by a  $T_2$  identical to that of Eq. (4.3) or (4.5). A temperature dependent shift is also found as a phase shift of  $\rho_{12}(t)$ . This ascertains that the results obtained from coherent optical experiments may be directly related to those obtained from "slow passage" absorption studies.

## V. REDFIELD VERSUS MODIFIED BLOCH EQUATIONS

As the basic Redfield equations (3.5) and (3.7) look very similar to the modified Bloch equations as postulated by McConnell,<sup>19</sup> it seems appropriate to make a comment here. Although Eqs. (3.7a) and (3.7b) describe exchange of coherence, this only occurs as a *feeding* process. This is in contrast to McConnell's postulate, where exchange is a combination of feeding and decay. In order to get this combination of feeding and decay from our formalism, we must demand, that  $\Gamma_{12-34}(\Gamma_{34-12})$  equals  $\Gamma_{12}(\Gamma_{34})$ . From the discussion of these decay constants in Sec. III, it is concluded that, in the absence of radiative and radiationless decay, this is only the case, when (a) near-resonant (within the linewidth) transitions are considered [(3.10)], (b) the role of secular interactions (Raman scattering of bandphonons) is negligible ( $\Gamma_{ij}^A \ll \Gamma_{ij}^{NA}$ ), and finally (c) the scattering amplitudes in the ground and excited state are identical. From these conditions and using (3.13)–(3.15) we then derive the following relations:

$$\begin{aligned} \Gamma_{12-34} &= \Gamma_{12} = \Gamma_{1-3} = \Gamma_{2-4} = W^+ = W, \\ \Gamma_{34-12} &= \Gamma_{34} = \Gamma_{3-1} = \Gamma_{4-2} = W^- = \tau^{-1}, \end{aligned} \quad (5.1)$$

and

$$W\tau = \exp[-(\hbar\Omega/kT)]. \quad (5.2)$$

In (5.1) and (5.2) we have also given the notation used by van 't Hof and Schmidt<sup>18</sup> and Harris<sup>17</sup> in using modified Bloch equations and exchange theory. The models used by these authors are therefore applicable only in situations where conditions (a)–(c) warranted.

With identities (5.1) the population transfer among the four levels may be expressed as an exchange of population *inversion*, with the same rates as those for the exchange of coherence. This is in accordance with a second implicit assumption of McConnell. Under these limiting conditions the Redfield equations change into the modified Bloch equations:

$$\begin{aligned} (\dot{\rho}_{22} - \dot{\rho}_{11}) &= -W(\rho_{22} - \rho_{11}) + \tau^{-1}(\rho_{44} - \rho_{33}), \\ (\dot{\rho}_{44} - \dot{\rho}_{33}) &= -\tau^{-1}(\rho_{44} - \rho_{33}) + W(\rho_{22} - \rho_{11}), \\ \dot{\rho}_{12} &= -i(\omega_{12} + \Delta_{12}/\hbar)\rho_{12} - W\rho_{12} + \tau^{-1}\rho_{34}, \\ \dot{\rho}_{34} &= -i(\omega_{34} + \Delta_{34}/\hbar)\rho_{34} - \tau^{-1}\rho_{34} + W\rho_{12}. \end{aligned} \quad (5.3)$$

For the description of triplet spin<sup>18</sup> and Raman<sup>20</sup> dephasing, assumption (c) seems justified, as all scattering processes occur within one electronic state. For the description of optical dephasing processes, however, this assumption is questionable. In fact, the scattering amplitudes in the ground and excited electronic state in general will be different (Fig. 1).

## VI. COMPARISON WITH OTHER LINE SHAPE THEORIES

### A. Introduction

In the previous section it was shown how the modified Bloch equations, as used by Schmidt and van 't Hof, derive from the Redfield equations, when the scattering amplitudes in the ground and excited state are identical. The expression for the frequency behavior of the optical polarization was deduced from the dynamical equations (4.1) or (5.3) by insertion of the slow passage solutions into the polarization formula

$$\langle\mu\rangle = \text{Tr}\rho\mu. \quad (6.1)$$

In this section line shape theories will be discussed, in which the polarization  $\langle\mu\rangle$  instead is calculated directly from linear response theory.<sup>33,34</sup> In this theory a weak semiclassical optical field, adiabatically switched on at  $t = -\infty$  and suddenly switched off at  $t = 0$ , induces a polarization into the system which is linear in the field

$$\langle\mu\rangle = X(\omega)E(t), \quad (6.2)$$

where  $X(\omega)$  is the susceptibility. The absorption (A) is given by

$$A = \frac{1}{2}\omega X''(\omega)|E|^2, \quad (6.3)$$

where  $X''(\omega) = -\text{Im}X(\omega)$ . The line shape formula within this formalism is

$$A(\omega) = \omega X''(\omega) = (\omega/\hbar) \text{tgh}(\hbar\omega/2kT)I(\omega), \quad (6.4)$$

where

$$I(\omega) = \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \mu^*(0) \mu(t) \rangle_0. \quad (6.5)$$

Here  $\mu(t)$  is the interaction representation for  $\mu$  in relation to the total Hamiltonian  $H(t) = H - \mu^* E$ , or the Heisenberg representation with respect to  $H$ . ( $H$  is the Hamiltonian characterizing the system.) The brackets  $\langle \rangle_0$  denote averaging over the initial ensemble (without the external field). In the line shape formula (6.5) the field is absent, so that saturation effects are not incorporated.

Apart from a trivial change of  $i$  into  $-i$ , the operator  $\mu$  will obey the same differential and master equation as the reduced density operator<sup>26</sup> and in the most general case its time dependence will be governed by both adiabatic and nonadiabatic rates, as described in Sec. III. In order to actually calculate this time dependence the problem can be formulated in two different ways.<sup>36</sup>

In the fully quantum-mechanical treatment an intrinsically time independent Hamiltonian is used of the general type:

$$H = H_0 + F + H_1. \quad (6.6)$$

Here  $H_0$  depends only on the molecular variables (and the time in the presence of a radiation field) and gives rise to the peaks in the molecular spectrum.  $F$  is the energy due to other degrees of freedom and does not contribute new spectral peaks, i.e.,

$$\begin{aligned} [H_0, F] &= 0 \\ [\mu, F] &= 0. \end{aligned} \quad (6.7)$$

$H_1$  is the interaction energy of the molecule with its surroundings and

$$[H_1, F] \neq 0. \quad (6.8)$$

This is the way of attack of the problem in what we call the correlation function approach, where the fluctuations in  $\mu(t)$  are calculated by adopting a particular microscopic model for the Hamiltonian, which appears in the expression:

$$\mu(t) = e^{iHt/\hbar} \mu e^{-iHt/\hbar}. \quad (6.9)$$

Comparing the Refield-Hamiltonian (2.9) with (6.6), it is immediately obvious that the correlation function approach lends itself to a direct comparison with our model (Sec. VIC).

Alternatively, however, the problem could be formulated in terms of a time-dependent Hamiltonian:

$$H = H_0 + H_1(t), \quad (6.10)$$

where the time dependence of  $H_1(t)$  in (6.10) arises from the fact that in (6.6) the interaction  $H_1$  is affected by  $F$  through (6.8). In this respect  $F$  can be considered as a "Hamiltonian of motion," though in this approach  $F$  is not explicitly dealt with (semiquantum-mechanical theory).

In the isolated impurity model that we are considering,  $F$  corresponds with the Hamiltonian for the heatbath, inducing intramolecular exchange (next section). More

generally any Hamiltonian  $F'$  with properties defined by (6.7) and (6.8) will induce a time-dependent interaction  $H_1(t)$ , such as an intermolecular exchange interaction in the case of nonisolated impurities or of excitons.<sup>17,20</sup>

Now the differences in the various stochastic line shape theories relate to assumptions made about the fluctuations of  $\mu(t)$  caused by the above mentioned time-dependent interactions. Note that both methods of attack have counterparts in energy transfer theory, where the Grover-Silbey<sup>48</sup> and the Haken-Strobl-Reineker<sup>49,50</sup> theory parallel, respectively, the correlation function and stochastic approach. We now arrive at a discussion of both approaches, applied to the problem of intramolecular exchange induced by the heatbath.

## B. The stochastic approach

The starting point in the stochastic theory of line shape<sup>21-26</sup> is expression (6.5) for the spectral density

$$I(\omega) = \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \mu^*(0) \mu(t) \rangle, \quad (6.5)$$

where  $\langle \mu^*(0) \mu(t) \rangle$  is the correlation function of the transition dipole moment. Here  $\mu(t)$  is time dependent through  $H_1(t)$  of (6.10).

Although both secular and nonsecular effects of  $H_1(t)$  can be incorporated in the equation of motion for  $\mu(t)$ ,<sup>23-26</sup> the most popular version of the stochastic theory is the frequency-modulation model, introduced by Anderson and Weiss.<sup>21,22</sup> They pointed out, that due to the secular part of the perturbation (diagonal in the molecular eigenstates) a modulation of the transition frequency is introduced, so that  $\mu(t)$  can be expressed as

$$\mu(t) = \mu(0) \exp \left[ i \int_0^t \omega_0(t') dt' \right]. \quad (6.6)$$

Here the effect of nonsecular interactions is ignored or at most accounted for in an approximate manner by the addition of a small shift due to these interactions in higher order.

Under this assumption the line shape takes the form

$$\begin{aligned} I(\omega) &= |\mu(0)|^2 \int_{-\infty}^{+\infty} dt e^{-i\omega t} \left\langle \exp \left[ i \int_0^t \omega_0(t') dt' \right] \right\rangle, \\ &= |\mu(0)|^2 \int_{-\infty}^{+\infty} dt \exp[-i(\omega - \omega_0)t] \\ &\quad \times \left\langle \exp \left[ i \int_0^t \Delta\omega(t') dt' \right] \right\rangle, \end{aligned} \quad (6.7)$$

where the brackets  $\langle \rangle$  now denote averaging over the frequency fluctuations. Its calculation therefore reduces to that of the correlation function

$$\varphi(t) = \left\langle \exp \left[ i \int_0^t \omega_0(t') dt' \right] \right\rangle, \quad (6.8)$$

by adopting a particular modulation model<sup>47</sup> (Gauss, Markov). This approach to the line shape has been very successful in explaining exchange and motional narrowing phenomena in magnetic resonance, as discussed in great detail by Kubo and co-workers.<sup>23-25</sup>

McCumber<sup>27</sup> was the first one who noticed that this theory is closely related to the theory describing ZPL's in optical impurity spectra. He noted that a continuum of possible frequency shifts is available for an optical transition due to quadratic electron-phonon coupling with low frequency band phonons. From the fully quantum-mechanical treatment of Sec. III, however, we would call the effect of the band phonons an optical dephasing a secular decay rather than exchange, as only one transition is involved.

A situation that more closely describes exchange is that where the transition frequency can jump to several discrete values at a random rate. When it is assumed that this random modulation can be described by a Markoffian process<sup>22,26</sup> a line shape can be calculated without great difficulties.<sup>22</sup>

Harris<sup>17</sup> recently used such a picture to explain optical dephasing of Frenkel excitons and (by implication) of ZPL's in mixed crystals. Applied to a four-level system this theory yields the following expression for the line shape:

$$I(\omega) = \frac{-W^* \Delta^2 / (1 + W^* \tau)}{(\omega_0 - \omega)^2 (\omega_0 + \Delta - \omega)^2 + [W^* (\omega_0 + \Delta - \omega) + \tau^{-1} (\omega_0 - \omega)]^2} \quad (6.9)$$

Comparing the width and shift of this line shape function with those [(4.3) and (4.4)] calculated from the optical Redfield equations we find that they are identical, in the limit:

$$\Gamma_{12-34} = \Gamma_{12} = W^*$$

and

$$\Gamma_{34-12} = \Gamma_{34} = \tau^{-1} \quad (5.1)$$

In other words, the "slow passage" solutions for  $\tilde{\rho}_{12}$  and  $\tilde{\rho}_{34}$  of the modified Bloch equations, lead to a line shape function  $\text{Im}(\tilde{\rho}_{12} + \tilde{\rho}_{34})$  which is identical to the one calculated from a stochastic (Markoffian) line shape theory. This point was not recognized in Ref. 17, where was stated that "the modified Bloch equations are the zero-temperature limit of the general exchange equations."

The source for really serious shortcomings of the stochastic theories is the fact that the heatbath is not explicitly dealt with, as we already remarked in the previous section. As a consequence, in these theories, resonant (within the linewidth) and nonresonant coherence transfer is treated on equal footing. From the results of Sec. III, however, it is easily shown that nonresonant coherence transfer can only occur when the initial and final state scatter to different heatbath states. This process is less probable and, couched in the language of perturbation theory, only occurs in third and fourth order.

Another consequence is that the jump rates induced by the "motional" Hamiltonian are easily misinterpreted; it is only by the fully quantum-mechanical treatment of exchange that these rates are understood in terms of interference of nonsecular scattering processes. Note, that in this respect nonsecular interactions can never be ignored, in contradiction to the assumption in the random-frequency model of exchange.

### C. The correlation function approach

In the correlation function approach to the line shape of a ZPL a particular model Hamiltonian is required, as we already remarked above. In Sec. II we described a model for an isolated impurity within a phonon reservoir which in essence is the one that Krivogla<sup>31</sup> takes as a starting point for his line shape theory. Both Krivogla<sup>28-30</sup> already in 1964 pointed out that the line shape obtained in the adiabatic BO approximation is substantially modified when anharmonicity of the phonons is included. Krivogla<sup>31</sup> also emphasized the special role of localized phonons, both without<sup>31</sup> and with<sup>32</sup> non-BO coupling.

To discuss these theories we return the Hamiltonian (2.7)

$$H = H_e + H_p + H_{e-p}, \quad (2.7)$$

to calculate the spectral density  $I(\omega)$  of Eq. (6.5). In the Condon approximation we may write

$$\mu = \mu_{0f} a_f^* + \mu_{0f}^* a_f, \quad (6.10)$$

where  $\mu_{0f}$  is the electronic transition dipole moment. Substituting (6.10) in (6.5) yields<sup>16</sup>:

$$I(\omega) = |\mu_{0f}|^2 \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \langle a_f(0) a_f^*(t) \rangle \rangle, \quad (6.11)$$

where we replaced  $\langle \rangle_0$  by the double brackets to indicate that both quantum-mechanical and statistical averaging is required. In the low temperature limit this averaging procedure is performed over the unexcited impurity only and over the (anharmonic) phonon reservoir.

As  $H_{e-p}$  contains the electron-phonon interaction that only affects the excited impurity, we can write for the initial Hamiltonian ( $H_i$ ) describing the unexcited impurity:

$$H_i = H_e + H_p = H_e + H_p^0 + H_{anh}. \quad (6.12)$$

When substituting (6.12) in (6.11) we arrive at

$$I(\omega) = |\mu_{0f}|^2 \int_{-\infty}^{\infty} dt \exp[-i(\omega - \omega_{f0})t] \times \langle \exp(iHt/\hbar) \exp(-iH_i t/\hbar) \rangle_{th} \quad (6.13)$$

where  $\omega_{f0} = \omega_f - \omega_0$  and  $\langle \rangle_{th}$  denotes averaging over the thermal (anharmonic) heatbath only. (Compare 6.7.) The line shape is found by calculating the Fourier transform of the thermal correlation function<sup>28-32</sup>

$$e^{e^{(t)}} = \langle \exp(iH_f t/\hbar) \exp(-iH_i t/\hbar) \rangle_{th} = \left\langle \exp_T i/\hbar \int_0^t H_{e-p}(\tau) d\tau \right\rangle_{th}. \quad (6.14)$$

In the last equality<sup>51</sup>  $H_{e-p}(\tau)$  is the interaction representation of  $H_{e-p}$  in relation to  $H_i$  and  $\exp_T$  is a time-ordered exponential. Considering the explicit form of the interaction ( $H_{e-p}$ ) given in (2.7), one notes that it only contains electron-phonon coupling and *not* the anharmonicity of the pseudolocalized phonon, which according to our model, is essential for coherence transfer. Therefore, the averaging over the anharmonic ensemble of only these correlation functions which have values in the har-

monic approximation, will only result in a modification of the usual (harmonic) expressions for the Raman scattering contribution to the ZPL.

For the contribution of a pseudolocalized phonon to optical dephasing of the ZPL Krivogla<sup>31</sup> calculates a Lorentzian line shape, with a temperature dependent shift ( $\Delta_T$ ) and width ( $\gamma_T$ ), given by

$$\Delta_T = V_{\kappa\kappa'} \bar{n}_\kappa, \quad (6.15)$$

(Compare (2.16))

$$\gamma_T = \sum_{\kappa} (|\bar{V}_{\kappa\kappa'}|^2 / \Gamma_{\kappa}) \bar{n}_\kappa (\bar{n}_\kappa + 1), \quad (6.17)$$

where  $\kappa$  runs over all pseudolocalized phonons.  $V_{\kappa\kappa'}$  is the amplitude for quadratic electron pseudolocal phonon coupling;  $\Gamma_{\kappa}$  is the pseudolocal anharmonic width. These results were obtained in the limit

$$h\omega_{\kappa} \gg \Gamma_{\kappa} \gg V_{\kappa\kappa'} \gamma_T + \gamma_R + \gamma_{NR}. \quad (6.18)$$

We note here that this correlation function approach thus in essence only accounts for secular (adiabatic) phonon scattering events exactly as in the case of the stochastic theory of McCumber for the optical line shape. We also draw attention to the fact that at low temperature ( $\bar{n}_\kappa \ll 1$ ) and in the fast exchange limit of the stochastic line shape theory, the results of the correlation function approach and the stochastic theory for the line shape are formally identical.

We finally note that Abram in his description of optical dephasing<sup>16</sup> also neglects the effect of phonon anharmonicity. This again implies that only the contribution of secular perturbations to the optical line shape were investigated and the effects of coherence transfer have been ignored.

## VII. CONCLUSIONS

In this article we have presented a model for optical dephasing in molecular mixed crystals which has been derived using Redfield relaxation theory. The model considers an effective four-level system composed of an electronic ground and excited state and one pseudolocalized phonon level on the ground and excited state.

The scattering among the levels is shown to be induced by electron-phonon coupling and phonon anharmonicity and coherence transfer among the transitions is only shown to occur when the phonon anharmonicity dominates the electron-phonon coupling strength. In this limit the optical Redfield equations are shown to reduce to the modified Bloch equations. The interpretation, however, of the exchange term as a scattering interference effect remains mandatory also in this limit.

It is further found that only near-resonant transitions show exchange of coherence.

When a comparison is made between the Redfield theory and the stochastic and correlation function theories we conclude that in these latter theories, exchange processes are not properly taken into account. While from the Redfield theory it follows that exchange is due to *nonsecular interfering* perturbations among the levels which participate in the scattering, the correlation function theory, using the same Hamiltonian and basis set,

only considers coherence decay due secular perturbations. The stochastic theory ignores its interference character, and consequently ignores the near-resonance condition of both exchanging transitions. One thus has to be rather careful in using these latter theories, especially when experimental results, on basis of formulas derived, are being interpreted.

In conclusion we would like to point out that the theory presented here rests on the assumption that pseudolocalized phonons may be treated on equal footing with the impurity electronic states. In the text we have given experimental evidence which supports this approach. Whether this treatment has general validity in molecular mixed crystals will only become clear when more and detailed experiments on the optical line shape of transitions in such solids become available.

*Note added in proof.* Very recently Jones and Ze-wail<sup>52</sup> have also reported on the subject of optical dephasing in the condensed phase. It is interesting to note that their conclusion on the point of the exchange contribution to the line shape function is similar to ours. We remark, however, in contrast to a statement made in Ref. 52, that the contribution of the optical phonon branch to optical dephasing<sup>16</sup> may well be distinguished from that of exchange by studying the optical dephasing characteristics of several different guests in the same host crystal.<sup>2,3</sup>

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